

1,149,726



PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Production of Polyether Diols using Water as a Telogen

We, THE GENERAL TIRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, of No. 1708 Englewood Avenue, Akron,

5 County of Summit, State of Ohio, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described 10 in and by the following statement:—

The present invention relates to a method for the production of hydroxy-terminated polyoxyalkylene diols and more particularly, to a method for producing liquid polyoxyalkylene diols.

15 It is an object of the present invention to provide a method for producing substantially hydroxy-terminated polyoxyalkylene diols.

It is another object of this invention to provide a process for producing relatively low molecular weight liquid polyoxyalkylene diols having a hydroxyl functionality of approximately 2.

20 These and other objects and advantages of the present invention will become more apparent to those skilled in the art from the following detailed description and examples.

Our United Kingdom Patent Specification No. 1,063,525 discloses a method of polymerising organic compounds having at least one ring of 2 or 3 carbon atoms and one oxygen atom in the presence of certain double metal cyanide complexes as catalysts. Our United Kingdom Patent Specification No. 35 1,063,526 discloses catalytic compositions suitable for use in such a method.

According to the present invention it has been discovered—that substantially hydroxy-terminated polyoxyalkylene diols can be produced by the polymerization of (1) epoxide and/or oxetane monomers with (2) water in the presence of (3) certain double metal cyanide complexes which have been treated with organic materials such as alcohols, ethers, esters and the like. Depending upon the amount of

water employed, the resulting polymers (hereinafter referred to as telomers) can vary from light oils to greases and solids having a hydroxyl functionality of about 2.

The organic cyclic oxides which can be telomerized in accordance with the process of this invention are 1,2-epoxides, oxetanes, 3-substituted oxetanes and 3,3-disubstituted oxetanes, having an oxygen-carbon ring in which an oxygen atom is joined to 2 or 3 carbon atoms in the ring which will open and telomerize with the same or other cyclic oxide monomers in the presence of the double metal cyanide complex catalyst and which have up to a total of 18 carbon atoms; that is to say, up to 3 carbon atoms in the ring and up to 15 carbon atoms in the side chains. These cyclic oxide monomers may also contain 1, 2 or more aliphatic double bonds. Preferably, the cyclic oxides contain only 1 aliphatic carbon-to-carbon double bond. The alkenyl, ether and halogen substituted derivatives (except easily ionized halogen) of these cyclic oxides also can be employed.

70 Examples of useful cyclic oxides which can be employed in the process of the present invention are ethylene oxide (1,2-epoxy ethane), 1,2-propylene oxide, 1,2-butene oxide, 1,2-hexene oxide, 1,2-dodecane monoxide, isobutylene oxide, styrene oxide, 1,2-pentene oxide, isopentene oxide, 1,2-heptene oxide, allyl glycidyl ether, isoheptene oxide, 1,2-octene oxide, methyl glycidyl ether, ethyl glycidyl ether, phenyl glycidyl ether, butadiene monoxide, isoprene monoxide, oxetane (1,3-propylene oxide), tolyl glycidyl ether, 3,3-dimethyl oxetane, 3-allyl-3-methyl oxetane, 3-vinyl - 3 - methyl oxetane, 1,2 - pentadecene oxide, 3 - butyl - 3 - decyl oxetane, 3-chloromethyl oxetane, and 3-chloromethyl-3-methyl oxetane.

75 It is preferred to employ the lower molecular weight oxides, such as ethylene oxide, propylene oxide, and the butylene oxides, containing from 2 to 12 carbon atoms.

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[Price 4s. 6d.]

The double metal cyanide complex catalysts which are useful in the process of this invention are prepared by reacting a transition metal cyanide complex with a metal salt in aqueous media. Removal of substantially all of the water present in the catalyst is desirable to enhance the activity of the catalyst although it would appear that removal of all the water is not practicable and may not be desirable. It has been found that most of the water can be removed and the activity of the catalyst further enhanced by treating the catalyst with a complexing or co-ordinating material such as an alcohol, ether, ester, sulfide, ketone or aldehyde.

In general, the double metal cyanide catalysts employed in the present invention have the following rational formulas:

$$M_a[M'(CN)_b]_c \text{ and/or } M_a[M'(CN)_b(X)_t]_c$$

wherein M is a metal ion which forms a metal-oxygen bond that is relatively more stable than the co-ordinate bond between the metal and nitrogen atoms of the cyano, CN, group. On the other hand, M' is a transition metal ion that has more than 1 stable valence form and forms a relatively strong covalent bond with the carbon atom of the cyano group. An individual catalyst can contain more than one type of the M or M' metal ion in its structure.

The grouping of these metals, with the cyanide ion sharing electrons with the 2 metal ions, usually exists in polymeric form as follows:

$$(-M'-CN \dots M \dots NC-M')_n$$

wherein n is an integer of at least 1, and super three-dimensional polymers can be formed depending upon the co-ordination numbers of M and M'. Moreover, those metal ions which produce active cyanide catalysts can all co-ordinate with 6 groups (such as hexacyanoferrate (III)). Most of the hexacyanoferrates-(III), including zinc hexacyanoferrate(III), have a cubic face-centered lattice.

The CN⁻ group in the catalyst molecule is the bridging group. However, other bridging groups can be present in the catalyst molecule so long as the catalyst molecule contains at least a majority of CN⁻ bridging groups. Thus, r and t are numbers and r is greater than t. t is 0 when the CN⁻ group only is the bridging group. Other bridging groups, X in the formula above, which can be present with the CN⁻ group, can be at least one of the following: F⁻, Cl⁻, Br⁻, I⁻, OH⁻, NO, O²⁻, CO, H₂O, NO₂⁻, C₂O₄²⁻, SO₄²⁻, CNS⁻, CNO⁻, NCO⁻, and NCS⁻.

In the above formulas M is at least one metal selected from Zn(II), Fe(II), Fe(III), Co(II), Ni(II), Mo(IV), Mo(VI), Al(III), V(IV), V(V), Sr(II), W(IV), W(VI), Mn(II), and Cr(III). On the other hand, M' is at least one metal selected from Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), V(IV) and V(V). Also a, b and c are numbers whose values are functions of the valences and co-ordination numbers of M and M', and the total net positive charge on M multiplied by a should be essentially numerically equal to the total net negative charge on [M'(CN)_b] or [M'(CN)_b(X)_t] multiplied by c. In most instances b and the sum of r+t corresponds to the co-ordination number of M' and is usually 6.

Examples of catalysts which fall within the above description and which may be employed in the process of the present invention are zinc hexacyanoferrate (III), zinc hexacyanoferrate (II), nickel (II) hexacyanoferrate (II), nickel (II) hexacyanoferrate (III), zinc hexacyanoferrate (III) hydrate, cobalt (II) hexacyanoferrate (II), nickel (II) hexacyanoferrate (III) hydrate, ferrous hexacyanoferrate (III), cobalt (II) hexacyanocobaltate (III), zinc hexacyanocobaltate (II), zinc hexacyanomanganate (II), zinc hexacyanochromate (III), zinc iodopentacyanoferrate (III), cobalt (II) chloropentacyanoferrate (II), cobalt (II) bromopentacyanoferrate (II), iron (II) fluoropentacyanoferrate (III), zinc chlorobromotetracyanoferrate (III), iron (III) hexacyanoferrate (III), aluminium dichlorotetracyanoferrate (III), molybdenum (IV) bromopentacyanoferrate (III), molybdenum (VI) chloropentacyanoferrate (II), vanadium(IV)hexacyanochromate(II), vanadium(V)hexacyanoferrate(III), strontium(II)-hexacyanomanganate(III), tungsten(IV)hexacyanovanadate(IV), aluminium chloropentacyanovanadate(V), tungsten(VI)hexacyanoferrate(III), manganese(II)hexacyanoferrate(II) and chromium(III)hexacyanoferrate(III). Examples of other cyanide complexes which can be employed are

$$\begin{aligned} &Zn[Fe(CN)_5NO], Zn_3[Fe(CN)_5NO_2]_2, \\ &Zn[Fe(CN)_5CO], Zn[Fe(CN)_5H_2O], \\ &Fe[Fe(CN)_5OH], Cr[Fe(CN)_5NCO], \\ &Cr[Fe(CN)_5NCS], Al[CoCN]_2, \text{ and } \\ &Ni_3[Mn(CN)_5CNS]_2 \end{aligned}$$

Mixtures of the above compounds can also be employed.

In general, the complex catalysts of this invention are prepared by reacting aqueous solutions of salts which give a precipitate of a metal salt of a transition metal complex anion. For example,

$$M_aZ + M''[M'(Y)]_n \rightarrow M_a[M'(Y)]_n + M''Z$$

wherein M is a metal ion which precipitates complex anion salts, for example, Zn⁺⁺. a, b and c in the above equation are integers but do not necessarily have the same values on both sides of the equation since their values are functions of the valences and co-ordination numbers of M, M', M'' and possibly Y and Z. Z is a halide or other anion, for example,

Cl⁻. M'' is a hydrogen ion or a metal ion whose complex anion salts are soluble in water or other solvent, for example K⁺ or Ca⁺⁺. M' is a complexing transition metal ion, for example, Fe⁺⁺⁺. Y is a complexing anion, for example, CN⁻. In producing the complex cyanide catalyst useful in the present invention, an excess of M_aZ is usually desired.

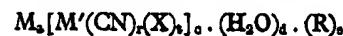
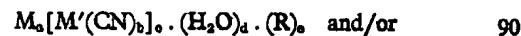
Apparently extraneous ions in the solution used to form the precipitate are easily occluded with the complex. Anions (Cl⁻, etc.) co-ordinate to the positively charged metallic ions in the lattice, and cations (K⁺) co-ordinate to the negatively charged nitrogen atoms of the cyanide bridging groups. These ions, especially those anions co-ordinating to or associated with the M atom, inhibit catalytic activity or prevent the complex from causing appreciable polymerization. Additionally, these ions, for example, easily ionizable Cl, may terminate the polymer chain.

To obtain a catalyst having the highest activity or the telomerization, an organic complexing agent is added to the catalyst precipitate preferably before it is centrifuged or filtered. This complexing agent can be mixed with the water during washing of the precipitate. It can be employed alone as the washing media provided the complexing agent is able to replace or dissolve the occluded ions, or it can be employed to treat or wash the precipitate after the precipitate has been washed with water, to replace at least a portion of the water. Sufficient complexing agent is employed to effect these results in order to enhance the activity of the catalyst. Such complexing agent should desirably co-ordinate with the M element or ion and should be a relatively low molecular weight organic complexing agent. The complexing agent should preferably be water-miscible or -soluble or substantially so, have a substantially straight chain and may contain up to 18 carbon atoms. Preferably, the complexing agent contains only up to 10 carbon atoms and is a liquid at room temperature.

Examples of complexing agents which can be employed in the double metal cyanide catalysts are alcohols, aldehydes, ketones, monoethers, diethers, polyethers and acyclic aliphatic polyethers. The alcohols are, for example, methanol, ethanol, propanol, isopropanol, butanol, octanol or octadecanol. The aldehydes are, for example, formaldehyde, acetaldehyde, butyraldehyde, valeric aldehyde, glyoxal, benzaldehyde, or toluic aldehyde. The ketones are, for example, acetone, methyl ethyl ketone, 3-pentanone or 2-hexanone. Examples of the cyclic ethers are dioxane, trioxethylene and paraldehyde. Aliphatic saturated monoethers, diethers, polyethers and acyclic aliphatic polyethers are also useful as treating agents; such ethers are, for example, diethyl ether, 1-ethoxy-pentane, bis-(β -chloroethyl) ether, dibutyl ether, ethyl propyl ether, bis-(β -methoxyethyl) ether, ethylene glycol dimethyl ether, tri-

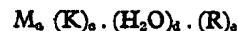
ethylene glycol dimethyl ether, dimethoxy methane, acetal, methyl propyl ether, diethoxy methane, or octaethylene glycol dimethyl ether. The acyclic polyethers are preferred. Still other complexing agents which can be employed are, for example, amides, esters, nitriles and sulfides, of which the following are examples: formamide, acetamide, propionamide, butyramide, valeramide; amyl formate, ethyl formate, hexyl formate, propyl formate, methyl acetate, ethyl acetate, and triethylene glycol diacetate; acetonitrile and propionitrile; dimethyl sulfide, diethyl sulfide, dibutyl sulfide and diamyl sulfide. Ethers having more than 1 oxygen atom and which form a chelate with respect to the metal M are preferred. Mixtures of these organic complexing agents can also be employed. Where there is an excess of that required to complex with the metal catalyst, the excess can be removed by extraction with a hydrocarbon solvent, such as pentane or hexane.

After treating with the organic complexing agent, the catalysts have the following rational formulas:



wherein d is 0 or a number which may be a fraction and e is 0 or a number which may be an integer or a fraction, since the catalyst is a nonstoichiometric complex in which various amounts of water and the R groups may be bonded to the various metals, e is 0 when the catalyst is not treated with the complexing agent R is one or more of the complexing agents such as the organic amides, alcohols, aldehydes, esters and ethers as herein above set forth. M, M', X, a, b, c, r and t have the same meaning as herein above set forth. In general, d and e will have values corresponding in part to the co-ordination number of M. However, both the H₂O and R can be occluded in the crystal lattice. In general the sum of the oxygen, nitrogen and/or sulfur or other co-ordinating atoms of H₂O and R (depending on the organic complexing agent) is equal to from about 0.1 up to about 5.0 g-atoms maximum per g-atom of M. If the catalyst is subsequently heated and dried to remove all of the water and/or organic complexing agents, the resulting product exhibits a loss or a substantial decrease in its catalytic activity.

As shown in the above formulas, if the organic complexing material is not used, R will not be present and thus e will equal 0. Thus, a formula for these catalysts is



wherein M, R, a, c, d and e have the above-identified meanings and wherein K is selected from M' (CN)_b and M' (CN)_b(X)_c and where

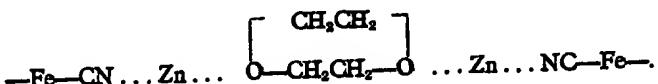
M' , X , b , r and t have the above-identified meanings. In the above formulas, the subscripts may represent whole numbers as well as fractional numbers.

5 In the preparation of the catalyst it is to be noted that where the catalyst is filtered or centrifuged from the solution in which it was prepared and then washed with one of the polymerizable cyclic oxides, such as propylene oxide, it contains little or no catalytic activity. For the subsequent polymerization of such monomers in order to obtain a storage stable catalyst for the polymerization of the cyclic oxide, the catalyst should be filtered or centrifuged from the solution in which it was prepared and then washed with water and an ether or other organic complexing compound as herein above described and subsequently with one of the polymerization cyclic oxide monomers. This results in a very active catalyst species.

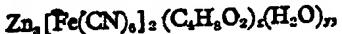
After the washing steps, the catalyst can be employed per se. However, it is preferred to dry the catalyst to remove excess treating agent and any remaining easily removable water and to provide for a more easily handled material. Such drying is accomplished by subjecting the catalyst to a vacuum or by heating the catalyst in air or in an inert atmosphere at a temperature up to about 100°C. It is preferred to dry the catalyst under a vacuum at low temperature (for example, 25°C at 0.5 to 1 mm Hg), or in a stream of air, nitrogen or inert gas at from 5° to 25°C. A heat-treated catalyst shows lesser activity and thus must be employed in higher concentration than the vacuum-treated catalyst. High temperatures are to be avoided since the catalytic activity of the catalyst is decreased as the temperature of drying is increased. It is believed that, at the high temperatures, some of the oxygenated or other organic complexing agents which are weakly co-ordinated to the metal M may be lost thereby leaving voids in the crystal lattice,

and the atoms in the crystal lattice may re-arrange to satisfy co-ordination requirements of the metals. Heating may also remove the cyanide ions, and reduce the metal M' . It is also possible that the molecular weight of the catalyst can increase thereby reducing the number of exposed metal ions on the surface of the catalyst and/or active sites. It is preferred to employ freshly prepared catalysts since the catalysts slowly decompose upon storage and thus reduce the catalytic activity. Where the catalyst is to be stored for long periods of time, it is preferred that they be stored at reduced temperatures to decrease the amount of decomposition.

While it is not precisely known what occurs to make the double metal cyanide complexes so useful in this polymerization, it is believed that the following takes places. While the following discussion relates to the treatment of the double metal cyanide catalyst with ethers, it will be appreciated that it is generally also applicable to the treatment with other organic complexing agents herein above set forth. It has been shown that, for example, with respect to zinc hexacyanoferrate which has been prepared by addition of aqueous zinc chloride solution to an aqueous solution of potassium ferricyanide, when the precipitate is washed with dioxane, a more effective catalyst is produced. During this treatment with dioxane it is believed that a number of reactions takes place: (1) some of the chloride ions in the lattice are oxidized, resulting in the reduction of Fe(III) to Fe(II); (2) the chlorine from reaction (1) reacts with the water and ether present during the wash-treatment to give Cl^- and chlorinated ether; (3) the successive washes remove some of the products of reaction (2); and (4) the oxygen atoms of the ether apparently co-ordinate to the zinc ions in the lattice, rearranging the lattice structure by inserting dioxane groups between the zinc ions as follows:



90 Thus, in the case of some of the dioxane-zinc hexacyanoferrate complexes, elemental analyses revealed that they were apparently non-stoichiometric complexes having the formula



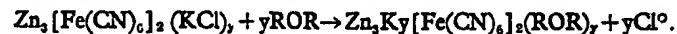
95 where $y=1$ to 2 and $x=2.5$ to 3.1. According to infrared and elemental analyses some of the dioxane in the complex may be chlorinated and some of the H_2O may be in the form of $-\text{OH}$ or $-\text{O}-$ groups. As ordinarily prepared, these complexes generally contained from about 4% to 5% of Cl^- and a smaller amount of K^+ .

If the catalyst is prepared with $\text{Zn}(\text{NO}_3)_2$ instead of ZnCl_2 , approximately 50% of the normal amount of dioxane is incorporated in the catalyst. This catalyst is not as effective as the one prepared from the chloride.

Although a great part of the iron in the ether (or other organic complexing moiety)-zinc hexacyanoferrate complex is believed to be Fe(II), as a result of the oxidation-reduction reaction that occurs during preparation, the dioxane complex prepared from ZnCl_2 and $\text{K}_4\text{Fe}(\text{CN})_6$ is not as active even at polymerization temperatures of 80°C. Analyses showed that a reduced amount of dioxane was incor-

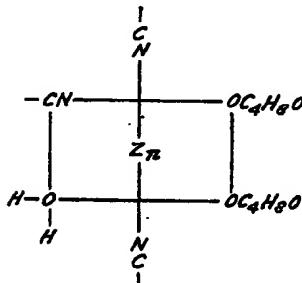
porated in such complexes and the chlorine content was high.

The reduced catalytic effect when using $Zn(NO_3)_2$ or $K_4Fe(CN)_6$ in the preparation of the catalyst complex is apparently related to the mechanism of the ether-hexacyanoferrate reaction. This mechanism may be viewed as



(Note: y in the above equation is a number and may not be the same as in the preceding formulas). The driving force for this reaction is the removal of Cl_2 by solution of the gas in the water and ether and the reaction of Cl_2 with the ether.

This oxidation-reduction reaction and displacement of the chlorine by ether is accompanied by a change in the crystal lattice. According to elemental and infrared analyses, most of the zinc ions in the lattice appear to form coordination bonds with from 1 to 2 oxygen atoms. The oxygen atoms of both the water and the ether are involved in this coordination. X-ray analysis and density measurements appeared to confirm this lattice change. Thus, the oxygen atoms of the ether compete with the CN groups of the $Fe(CN)_6$ anion to produce a polymeric structure with more exposed zinc ions as shown below:



This process of opening up the lattice is aided by the presence of water during the ether treatment. Apparently, the water dissolves the $Fe(CN)_6$ anion sections in the lattice that are coordinated with K^+ ions and more of the lattice thereby becomes exposed to the ether during the hexacyanoferrate-ether reaction.

The experiments have indicated that chloride ions can inhibit the polymerization of the cyclic oxide employed in the double metal cyanide complex catalyst. Thus, it is desirable to reduce the amount of ionizable chlorine or other ionizable anions in the catalysts. For example, the catalyst can be washed with an ether-water solution whereby the soluble chloride salt can be removed. In another method the zinc hexacyanoferrate is prepared by reacting compounds such as calcium ferricyanide, aluminium ferricyanide or lithium ferricyanide with zinc chloride and the chloride salt which forms can be removed by the ether during the washing

follows. As the chloride ions of the surface zinc ions in the crystal lattice transfer electrons into the $Zn \dots NC$ -Fe grouping, ether molecules can displace the resulting chlorine atoms and form ether-zinc coordinate bonds. For example,

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operation. It has also been found that when ions such as Cl^- are covalently bonded to the complexing catalyst, they apparently do not adversely affect the polymerization of the epoxides and oxetanes. In fact, chlorinated ethers have been found to improve the efficiency of the catalyst since it is believed that the halogenated ethers are more readily displaced by the epoxides and oxetanes to initiate polymerization.

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It is preferred to employ the polyethylene glycol ethers to treat the double metal cyanide since a very active catalyst is thereby obtained. Apparently a chelate bond is formed with the zinc ion thereby increasing the driving force of the hexacyanoferrate-ether reaction, whereby a very open lattice is produced since polymeric coordination through the oxygen atom is prevented. The use of the dimethyl or diethyl ethers of diethylene glycol was found to increase the efficiency of the catalyst. It thus appears that the most active catalysts for the cyclic oxide polymerization are those which contain the greatest amount of zinc-oxygen-ether bonds rather than zinc-oxygen-water bonds and the least amount of ionizable chlorine.

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The amount of catalyst employed can range from 0.001 to 15% by weight of the total weight of the telomerizable cyclic oxide monomers employed during telomerization. It is preferred to employ from about 0.01 to 1.0% by weight of the catalyst based on the total weight of the monomers.

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The amount of water employed as a telogen in the process of this invention is dependent upon the molecular weight of the polyoxyalkylene diol desired. The amount of water can vary from as low as .001% by weight to as high as 5.0% by weight based on the polymerizable oxide. Where molecular weights below 5,000 are desired, the amount of water should be about .4% and higher. This water is added in the propylene oxide and does not include any water that may be occluded in the catalyst. The cyclic oxide may be telomerized in bulk or in a solvent. The cyclic oxide should be telomerized under inert or non-oxidizing conditions, for example, under nitrogen, argon, neon, helium, krypton or other inert gas. The cyclic oxide can also be telomerized under pressure of the vapourized cyclic oxide.

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When large amounts of water are employed to yield low molecular weight telomers, it is preferred to add the water incrementally

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because large amounts of water decrease the rate of telomerization. Thus, in order to obtain practical rates of reaction, the water is added incrementally. The incremental addition of water can also be employed to give telomers of a broader molecular weight distribution than those possible where all of the water is added at the beginning of the reaction.

The telomerization is preferably conducted 10 in a closed container at atmospheric pressure or at pressure slightly greater than atmospheric. The pressure should be sufficient to maintain a liquid state for dispersion of the catalyst and heat transfer, although it is also possible to bubble gaseous cyclic oxide monomers into the solution for the telomerization.

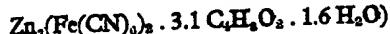
The temperature at which the process of this invention is conducted is not critical and can vary from about 0°C. to 125°C. or somewhat higher, preferably the temperatures from about 15°C. to 80°C. being employed. In some instances an induction period may be observed with the less active catalyst species.

The telomerized product in accordance with 25 the process of this invention can generally be extended by employing the organic diisocyanates such as toluene diisocyanate, *p*-phenylene diisocyanate, ethylene diisocyanate, trimethylene diisocyanate, dodecamethylene diisocyanate, butylene - 1,2 - diisocyanate, *m*-phenylene diisocyanate, benzene - 1,2,4 - tri-isocyanate or polymethylene polyphenyl isocyanate to yield polyurethane foams and elastomers. The polyurethane elastomers are 35 useful as gaskets, foot mats, shoe heels, engine mountings and the like. The polyurethane foams are useful as insulation and the like.

The following examples serve to further 40 illustrate the invention and are not to be construed as limitations thereon. In the examples all parts are by weight unless otherwise specifically stated.

EXAMPLE I

A zinc hexacyanoferrate-dioxane complex 45 catalyst (essentially



was prepared as follows: An aqueous solution (200 ml) of $\text{K}_4\text{Fe}(\text{CN})_6$ [0.430 Molar] was added slowly to 75 ml. of an aqueous solution 50 of zinc chloride (1.89 Molar). This is equivalent to a 10 mol% excess of zinc chloride. The precipitated zinc hexacyanoferrate was separated by centrifugation (2,000 RPM for 30 min.) and washed four times with 200-ml. portions of anhydrous, peroxide-free dioxane

and dried at 25°C. at less than 1 mm. Hg. overnight. It was employed to catalyze the polymerization of propylene oxide and allyl glycidyl ether in the presence and in the absence of water. 0.1 grams of the zinc hexacyanoferrate-dioxane complex and 0.1 grams of phenyl-beta-naphthylamine and air were charged into a dry, crown-capped, beverage bottle, containing a magnetic stirring bar. The bottle was flushed with nitrogen, capped and propylene oxide (47.1 grams, 0.81 moles) and allyl glycidyl ether (2.88 grams, 0.25 moles) were added by means of a hypodermic syringe. In the first instance the propylene oxide contained no water and in the second, the propylene oxide contained .00023 weight % water. The polymers obtained at the same conversion (93%) had intrinsic viscosities in isopropanol at 60°C. of 4.9 and 2.8 respectively. This shows the effect of water in reducing the molecular weight.

EXAMPLE II

In this example a zinc hexacyanocobaltate-acetone complex prepared as follows was employed as the catalyst. A solution containing 694 g. $\text{Ca}_2[\text{Co}(\text{CN})_6]_2$ and 505 g. water was added dropwise to a solution of ZnCl_2 (55.5 g.) in 63.2 g. water. Acetone (1895 g.) was then added to the slurry of the precipitate in water and the mixture was stirred for 15 minutes. The precipitate was separated by centrifugation (7000 RPM, 40 min.) and then washed ten times with 70 volume % acetone in water. Approximately 2000 ml. of solution was used for each wash. After two additional washes with 2000 ml. of pure acetone, the solid cake was dried at 25°C. at less than 20 mm. Hg. for 9-10 hours.

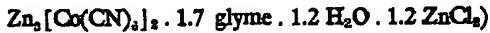
The general procedure for the telomerization reaction is as follows. The catalyst was charged into a dry beverage bottle, the bottle capped, evacuated and filled with nitrogen. A propylene oxide-water mixture (25 grams) was added by means of a hypodermic syringe. The bottle was then placed in a constant-temperature bath maintained at 80°C. and agitated in an end-over-end rotating assembly. The product was recovered by evaporating the propylene oxide. The pertinent data are summarized in Table I. The molecular weight was determined by vapor phase osmometry. The hydroxyl content was determined and the functionality was calculated by dividing the number of moles of the hydroxyl group by the number of moles of the telomer.

TABLE I

Experiments	Water in PO, Wt. %	Catalyst Wt. %	Time Hrs.	% Yield	Mol. Wt.	Functionality
A	0.18	0.02	2.5	92	8500	1.9
B	0.36	0.04	24	92	4000	2.1
C	0.54	0.16	22	70	2150	2.2
D	0.72	0.16	24	81	1450	2.3

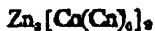
EXAMPLE III

The catalyst employed in this example was (essentially) prepared as follows:



was prepared as follows. An aqueous solution (100 ml.) of $K_3Co(CN)_6$ [0.296M] was passed through a bed containing the acid form of Amberlyst 15 (Registered Trade Mark). In this process H^+ was exchanged for K^+ . The acid solution was then evaporated at room temperature to a volume of 80 ml. resulting in a 0.370M solution of $H_2Co(CN)_6$, and the solution was then rapidly mixed with 10 ml. of an aqueous solution of $ZnCl_2$ [4.87M]. This is equivalent to using a 10 mol % excess of $ZnCl_2$. After the precipitation of 188ml.). The precipitate was finally recovered and dried at 25°C. at less than 1 mm. Hg. overnight. Glyme is the dimethylether of ethylene glycol.

The catalyst $Zn_3[Co(CN)_6] \cdot$ glyme was weighed out and placed in 12 ounce borosilicate glass bottles .08 g to each bottle, (All bottles were washed and rinsed in deionized water and dried at 200°C overnight). After charging the catalyst, the bottles were immediately capped and evacuated at less than 22 mm. Hg. pressure for 15 minutes. Propylene



25 was complete, 60 g. of glyme was added slowly to the aqueous slurry and stirred for 15 minutes. The precipitate was separated by centrifugation (7000 RPM, 40 min.) and then washed twice with glyme (total volume:

188 ml.). The precipitate was finally recovered and dried at 25°C. at less than 1 mm. Hg. overnight. Glyme is the dimethylether of ethylene glycol.

The catalyst $Zn_3[Co(CN)_6] \cdot$ glyme was weighed out and placed in 12 ounce borosilicate glass bottles .08 g to each bottle, (All bottles were washed and rinsed in deionized water and dried at $200^{\circ}C$ overnight). After charging the catalyst, the bottles were immediately capped and evacuated at less than 22 mm. Hg. pressure for 15 minutes. Propylene oxide (60 ml., 50 g) was then added and deionized water was then added by means of a syringe. The sample bottles were immediately placed into the safety can and placed in an $80^{\circ}C$ tumbling action bath. The pertinent data in this example is summarized in the following chart.

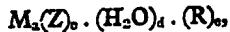
TABLE II

	A	B	C	D
Catalyst gm.	.08	.08	.08	.08
Propylene oxide gm.	50	50	50	50
Water, ml 1st addition	1.00	.35	.20	.20
2nd addition	—	.65	.80	.80
Total	1.00	1.00	1.00	1.00
time between 1st and 2nd addition of water	—	218 min.	100 min.	68 min.
Reaction times, hrs.	24	24	24	24
Temperature °C.	80	80	80	80
% Conversion	6.3	22.6	52.5	40.8
Hydroxyl Number	—	261	58.1	76.9

From the above data, it is evident that the incremental addition of water greatly improves the yield of the telomer.

WHAT WE CLAIM IS:—

- 5 1. A process for the preparation of polyoxyalkylene ether diols, wherein the hydroxyl groups are substantially terminal hydroxyl groups, which comprises admixing at least 1 polymerizable organic cyclic oxide monomer having a ring of 2 or 3 carbon atoms and 1 oxygen atom and up to a total of 18 carbon atoms, said oxide being selected from epoxides, oxetanes, 3-substituted oxetanes, and 3,3-di-substituted oxetanes, with water in an amount of from .0001 to 5.0% by weight based upon the polymerizable oxide, in the presence of a catalyst in an amount of from .001 to 15% by weight of said monomer, said catalyst comprising a double metal cyanide complex compound having the general formula
- 10
- 15
- 20



wherein Z is $M' (CN)_b$, or $M' (CN)_c X$; M is at least one metal selected from Zn (II), Fe (II), Fe (III), Co (II), Ni (II), Mo(IV), Mo(VI), Al(III), V(IV), V(V), Sr(II), W(IV), W(VI), Mn(II) and Cr(III); M' is at least one metal selected from Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), V(IV), and V(V); X is at least one of F^- , Cl^- , Br^- , I^- , OH^- , NO_3^- , CO_3^{2-} , H_2O , NO_2^- , $C_2O_4^{2-}$, SO_4^{2-} , CNO^- , CNS^- , NCO^- and NCS^- ; R is a low molecular weight organic compound having up to 18 carbon atoms and selected from alcohols, aldehydes, ketones, ethers, esters, amides, nitriles and sulfides; a, b, and c are numbers whose values are functions of the valences and the coordination numbers of M and M', the total net positive charge on M times a being essentially numerically equal to the total net negative charge on Z times c; r is a number, t is a number, r being greater than t; d is 0 or a number and e is 0

or a number, and maintaining said admixture at a temperature at which said water and cyclic oxide react to produce said polyoxyalkylene ether diols.

45 2. A process according to claim 1 wherein M is selected from the group consisting of zinc (II), nickel (II), iron (II) and cobalt (II) and mixtures thereof, and wherein M' is selected from the group consisting of iron (II), iron (III), cobalt (III) and chromium (III) and mixtures thereof.

50 3. A process according to Claim 1 or Claim 2 wherein the temperature is from about 0° to $125^\circ C$.

55 4. A process according to Claim 3 wherein the temperature is from 15° to $80^\circ C$.

60 5. A process according to any one of Claims 1 to 4 wherein the polymerization is conducted in the presence of a solvent for said monomer.

65 6. A process according to any one of Claims 1 to 5 wherein said catalyst is employed in an amount from .01 to 1% by weight of said monomer and wherein said water is employed in an amount of from 0.4 to 5.0% by weight of said monomer.

70 7. A process according to Claim 6 wherein the catalyst is a zinc cobalticyanide-ketone complex.

75 8. A process in accordance with Claim 6 wherein the catalyst is a zinc hexacyanoferrate cyclic diether complex.

9. A process in accordance with Claim 6 wherein the catalyst is a zinc cobalticyanide-acyclic polyether complex.

10. A process according to any one of claims 1 to 9 substantially as herein described and exemplified.

11. The product of a process according to any one of the preceding claims.

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